A hydrodynamic AFM flow cell for the quantitative measurement of interfacial kinetics

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A novel liquid flow cell is developed which allows atomic force microscopy images to be obtained under defined and modelled hydrodynamic flow conditions, enabling measured reaction fluxes to be compared with those calculated from proposed heterogeneous reaction mechanisms.

AFM of reacting surfaces has been carried out without defined flow conditions, for example by Hansma and coworkers[1] who observed that steps on a calcite surface under aqueous solution moved laterally as dissolution proceeded. This technique is extremely powerful since it can identify key structural features, for example steps or etch pits, which contribute to the dissolution process. This approach remains qualitative since no attempts have been reported in which quantitative measures of the reaction flux are related to a chemical model of the interfacial reaction. The latter dictates defined hydrodynamics and mass transport so that the variations of concentrations in space and time above the surface can be modelled.

The value of defined hydrodynamic conditions has been demonstrated by measurements in channel flow cells[2] in which a laminar flow of solution passed through a rectangular channel with a calcite crystal forming part of one wall. The reaction was monitored electrochemically by an electrode flush with the wall and immediately downstream of the calcite surface. Precise knowledge of the flow pattern enabled it to be shown that the reaction between H^+ and calcite was a first-order heterogeneous reaction of H^+. However, the channel geometry does not facilitate simultaneous observation of the changes in surface topography or a direct physical measurement of the rate of surface dissolution, since the insertion of a scanning probe would invalidate the analytic expression for flow velocities.

We have developed a novel flow cell, based on the standard Topometrix[3] Discoverer liquid immersion cell, in which AFM images may be obtained in the presence of a flowing liquid and in which the flow pattern may be calculated. The standard cell has tangential inlet and outlet ports at the periphery of a large irregular volume, so that the flow in the vicinity of the scanning cantilever is unpredictable. We have redesigned the cell by the addition of a new inlet port so that solution can be delivered through a precisely shaped and positioned stainless-steel duct directly to the front of the cantilever chip (Fig. 1). The liquid jet is aligned parallel to the front of the cantilever support chip and transverse to the cantilever. This gives a partly free field flow, not confined except by the sample below and the cantilever chip to one side, so the flow pattern is complex and is not amenable to an analytic solution. Such flow fields can however be solved using computational fluid-dynamics programs.

We report here preliminary studies in which the flow field was calculated by two-dimensional simulations, together with experimental data to demonstrate the validity of this design. Initial studies of an inclined jet using the FLOTRAN[4] and subsequently FIDAP[5] programs showed that a satisfactory flow field would be set up. In particular, it was confirmed that all of the solution reaching the surface of the sample will be fresh solution from the jet with no mixture or entrainment of the surrounding bulk solution, which is an essential requirement for full characterisation. Initial tests of the cell using a gold calibration microgrid also confirmed that AFM images could be obtained under flow conditions without detectable deterioration of image quality up to the highest flow rates used.

In the first study, the flow behaviour has been confirmed over a wide range of flow rates by determining the limiting current at a 1 × 1 mm platinum electrode which was placed in the sample position, Fig. 2. An aqueous solution of 5 mm potassium hexacyanoferrate(ii) with 1 m KCl was used, and the limiting current for the reversible one-electron oxidation to hexacyanoferrate(iii) determined for volume flow rates in the range 0.029 to 1.4×10^{-5} $cm^3\ s^{-1}$, with a stainless-steel jet of internal dimensions 0.057 × 0.057 cm.

The FIDAP simulation was based on a two-dimensional finite element model of a section of fluid 5.86 × 3.06 mm, including the cross-section of the jet tube and bounded below by the sample surface. The remaining boundaries represented the bulk fluid in the cell and permitted free flow. The model comprised 6564 elements of graded size, with a fine element mesh in regions of high gradients of velocity or of concentration, such as at the edges of the electrode. The simulation for a flow rate of 0.0014 $cm^3\ s^{-1}$ is shown in Fig. 2 as a streamline contour plot,

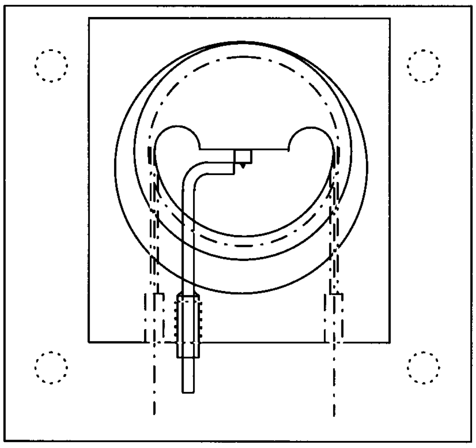

Fig. 1 Top view of the Topometrix sample cell showing the new inlet duct

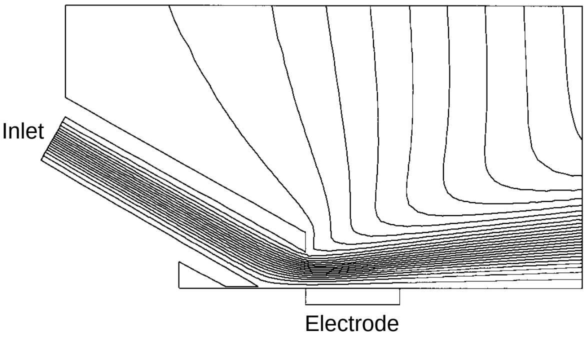

Fig. 2 The two-dimensional cross-section of solution modelled with FIDAP, showing jet and electrode positions, with streamline contours for a flow rate of 0.0014 ml s^{-1}

indicating that the jet flows near to the surface, moving away from it at a fairly shallow angle; as the flow rate is lowered, this angle increases and the jet broadens. The flux of hexacyanoferrate(II) to the electrode was calculated using FIDAP, by setting concentration boundary conditons of 5 mm at the inlet to the jet tube, and of zero, corresponding to the limiting current condition, at the electrode surface. Fig. 3 shows the simulated and the experimental limiting currents as a function of (flow rate)$^{1/2}$. For this two-dimensional approximation, it was assumed that the effective electrode width was 0.45 mm due to the narrower jet. On this basis good agreement was obtained over more than three orders of magnitude of flow rate, broadly confirming the simulated behaviour.

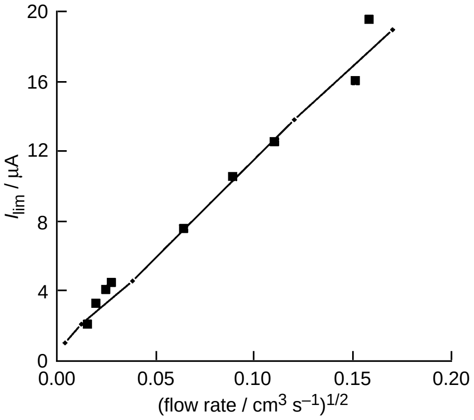

Fig. 3 Experimental (■) and simulated (—) limiting currents as a function of (flow rate)$^{1/2}$

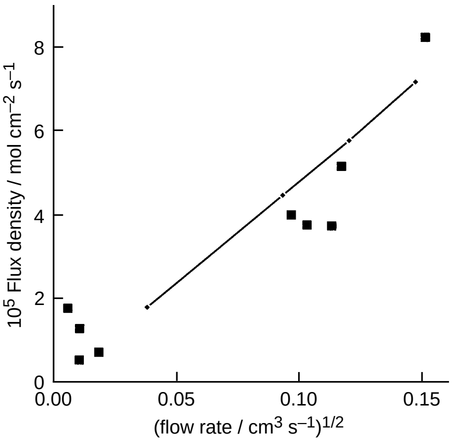

Fig. 4 Dissolution rate of calcite determined by AFM (■) and simulated (—) as a function of (flow rate)$^{1/2}$

The second study was the dissolution of a calcite surface in 0.98 mm aqueous HCl as a function of flow rate. By monitoring the change of the Z-piezo voltage during successive scans of the AFM image, the rate of recession of the surface and hence the flux of reacted material could be determined for different flow rates assuming a density of 2.71 g cm^{-3} for calcite. For the simulation (again two-dimensional), the dissolution reactions were expressed by eqns. (1)–(3) and the reaction flux at the scan location was calculated using the backward implicit finite difference (BIFD) method[6] with the rate constants $K_{\rm H_2CO_3} = 1.72 \times 10^{-4}$ m (this value is corrected for activity coefficients[2]), $k_3 = 20$ s^{-1}, and variable k_1, and with the fluid velocities taken from a FIDAP simulation. Fig. 4 shows the AFM determined flux rates together with the FIDAP/BIFD simulated values plotted against (flow rate)$^{1/2}$ for the case of $k_1 = 0.035$ cm s^{-1}.

$$\mathrm{H^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq)} \quad (1)$$

$$\mathrm{H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq)} \quad (2)$$

$$\mathrm{H_2CO_3(aq) \rightarrow H_2O + CO_2(aq)} \quad (3)$$

This is in excellent agreement with the value (0.043 ± 0.015) cm s^{-1} deduced from independent channel flow cell experiments[2] and confirms the validity of the hydrodynamic AFM approach.

We have shown that this novel design for an AFM flow cell is practicable and gives good agreement between experimental and calculated results using a two-dimensional finite element fluid-dynamics simulation of the complex flow field. A full three-dimensional flow simulation, while requiring substantial computer resources, should further improve accuracy, and work on this is in progress. This new cell should prove of value to AFM users for mechanistic investigations in many areas of solid/liquid reactions, allowing physical and structural changes to the surface to be related directly to proposed reaction mechanisms and rate constants.

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